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Kinetic Studies of Intermolecular Hydrogen Bonding in Carboxylic Acids by Means of Ultrasonic Absorption Measurement. I. Fatty Acids

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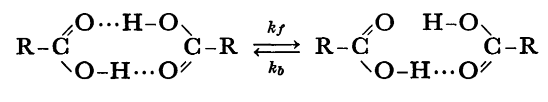
The ultrasonic absorptions in *n*-butyric, isobutyric, *n*-valeric, isovaleric, and *n*-caproic acids have been measured in the frequency range from 2.5 to 95 MHz in order to study the relationship between the ultrasonic absorption and the chemical structure of the alkyl group in carboxylic acids. The relaxation absorptions were observed for all the acids with relaxation frequencies in the range of 1.6—8.7 MHz. The kinetic parameters have been calculated on the basis of an assumption that the absorptions are associated with the breakage of one of the two hydrogen bonds in the dimer, as in the case of propionic acid. The values of the heat of reaction, ΔH, were calculated to be 4.7—6.4 kcal per mole of dimer. By an application of the results to Taft's equation, $\log K = \rho^*\sigma^* + sE_s$, it is deduced that the change in the ΔH in a series of monocarboxylic acids is due to variations in the inductive effect of each alkyl group. However, the change in the heat of activation, $\Delta H^{\neq}$, can not be explained in terms of the inductive effect.

It is well known that an excess absorption of ultrasound exists in the frequency range from 0.5 to 10 MHz in such liquid monocarboxylic acids as acetic[1,2] and propionic[3,4] acids. As the origin of this absorption, the transition from monomeric to dimeric molecules of carboxylic acid has been assumed.[5]

However, the ultrasonic investigation for acetic acid in various solvents by Piercy and Lamb[6] raises the question of whether the above mechanism for the ultrasonic absorption is reasonable for acetic acid. Furthermore, Tabuchi[7] has suggested that the absorption in acetic acid might be associated with the transition from the cyclic dimer to the open dimer. Also, one of the present authors[4] has concluded that the ultrasonic absorption is associated with a perturbation of the following equilibrium:



from his measurement of the ultrasonic absorption in methyl propionate solutions of propionic acid, and has calculated the kinetic parameters of this reaction.

Hitherto, the ultrasonic study of monocarboxylic acids has been done mainly for acetic and propionic acids. It is interesting to study the changes in the absorption with the increase in the carbon number and with the changes in the alkyl group of carboxylic acids in its structure.

Experimental

A pulse technique[4] was used to measure the ultrasonic absorption in the liquid monocarboxylic acids over the frequency range from 2.5 to 95 MHz. The velocity of the sound was measured by means of an ultrasonic interferometer[8] operated at 3.0 and 5.0 MHz. In order to observed the dependence of the relaxation frequency and the absorption on the temperature, measurements were made in the temperature range from 15 to 30°C for *n*-butyric, isobutyric, *n*-valeric, and isovaleric acids, and from 25 to 45°C for *n*-caproic acid. The relaxation absorption in *n*-caproic acid is relatively small in comparison with the others. The densities were measured with a pycnometer. An adiabatic-type calorimeter was used for the heat-capacity measurements. The chemicals used were all guaranteed grade and were used without further purification.

Results

The ultrasonic absorption spectra in a series of monocarboxylic acids are shown in Figs. 1—6. All the spectra can be represented by a single relaxation formula:

$$\frac{\alpha'}{f^2} = \frac{\alpha}{f^2} - B = \frac{A}{1+(f/f_{\max})^2} \qquad (1)$$

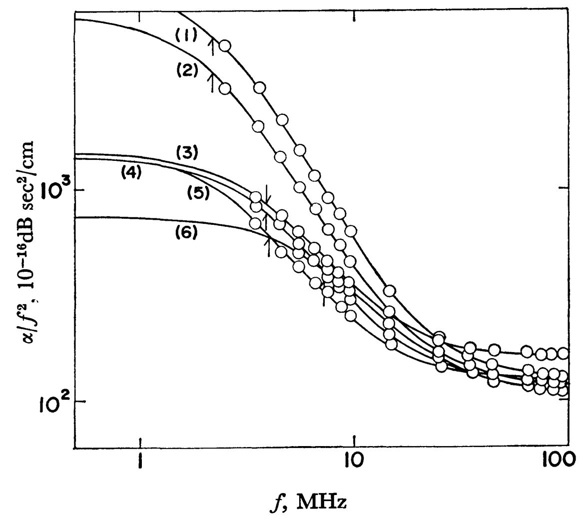


Fig. 1. Ultrasonic absorption spectra in monocarboxylic acids: (1), propionic; (2), butyric; (3), isovaleric; (4), valeric; (5), caproic; and (6), isobutyric acids at 25°C.

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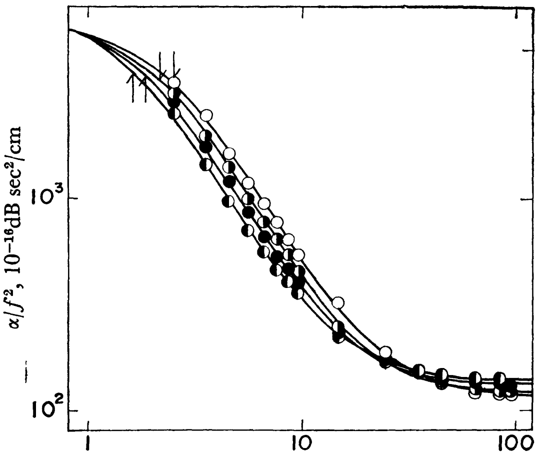


Fig. 2. Ultrasonic absorption spectra in butyric acid at various temperatutes: ◐: 15°C; ●: 20°C; ◑: 25°C; ○: 30°C.

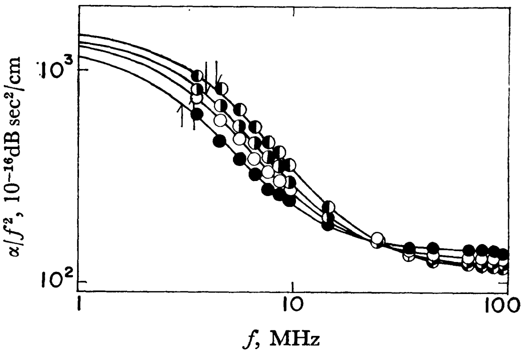


Fig. 3. Ultrasonic absorption spectra in valeric acid at various temperatures: ●: 15°C; ○: 20°C; ◑: 25°C; ◐: 30°C.

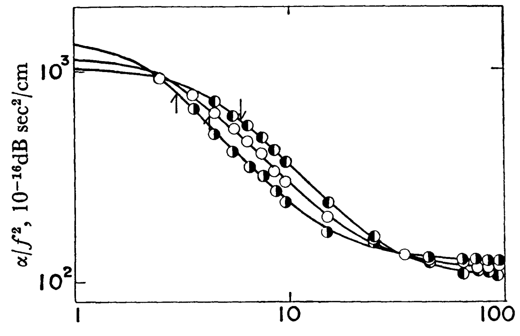


Fig. 4. Ultrasonic absorption spectra in caproic acid at various temperatures: ◑: 25°C; ○: 35°C; ◐; 45°C.

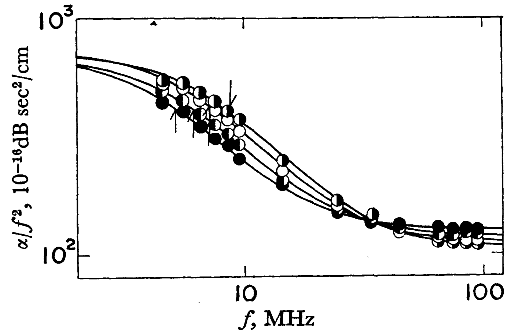
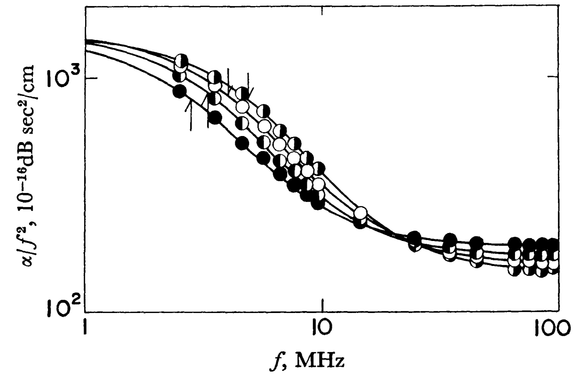


Fig. 5. Ultrasonic absorption spectra in isobutyric acid at various temperatures: ●: 15°C; ◐: 20°C; ○: 25°C; ◑: 30°C.



Fif. 6. Ultrasonic absorption spectra in isovaleric acid at various temperatures: ●: 15°C; ◐: 20°C; ○: 25°C; ◑: 30°C.

where α is the ultrasonic absorption coefficient; f, the frequency of sound; α', the excess absorption coefficient, and $f_{\max}$, the relaxation frequency. A and B are the excess and the classical absorption respectively. The values of A, B, $f_{\max}$, and the maximum of the absorption per wavelength $(\alpha'\lambda)_{\max}$ are listed in Table 1. The uncertainties in A, B, and $f_{\max}$ are approximately ± 10, ± 5, and $\pm 5\%$ respectively. The other values required for the calculation of kinetic parameters, such as the sound velocity (u), the density (ρ), the thermal expansion coefficient (l), and the heat capacity at a constant pressure (C_p), are given in Table 2. The errors in u, ρ, l, and C_p are ± 0.01, ± 0.05, ± 0.5, and

TABLE 1. THE ACOUSTICAL CHARACTERISTICS OF MONOCARBOXYLIC ACIDS AT THE VARIOUS TEMPERATURES

T (°K)	$f_{\max}$ (MHz)	A	B	$(\alpha'\lambda)_{\max}$ (10^{-2} dB)
		(10^{-16} dB·sec cm^{-1})		
		Butyric acid		
288	1.6	7600	137	7.6
293	1.9	7300	130	8.3
298	2.2	7000	118	9.1
303	2.5	6700	115	10.0
		Isobutyric acid		
288	5.2	580	125	1.8
293	6.4	572	117	2.1
298	7.3	623	109	2.6
303	8.7	600	104	2.9
		Valeric acid		
288	3.0	1120	140	2.1
293	3.4	1280	129	2.7
298	3.8	1300	118	3.0
303	4.4	1380	114	3.7
		Isovaleric acid		
288	2.8	1330	190	2.2
293	3.5	1200	173	2.7
298	4.2	1139	159	3.2
303	5.0	1090	126	3.7
		Caproic acid		
298	2.9	1400	124	2.5
303	3.6	1250	122	2.8
308	4.3	1110	112	2.9
313	5.0	1050	110	3.3
318	5.9	980	102	3.4

TABLE 2. THE THERMODYNAMIC PARAMETERS FOR THE MONOCARBOXYLIC ACIDS

T (°K)	u (3MHz) (10^5 cm sec^{-1})	ρ a) (g cm^{-3})	l b) (10^{-4} deg^{-1})	C_p^0 c) (cal g^{-1}· deg^{-1})
		Butyric acid		
288	1.2247	0.9634	9.77	0.526
293	1.2062	0.9584	9.77	0.526
298	1.1880	0.9534	9.77	0.526
303	1.1701	0.9485	9.77	0.526
		Isobutyric acid		
288	1.1747	0.9547	9.80	0.450
293	1.1562	0.9498	9.80	0.450
298	1.1363	0.9448	9.80	0.450
303	1.1179	0.9399	9.80	0.450
		Valeric acid		
288	1.2565	0.9430	8.82	0.590
293	1.2379	0.9386	8.82	0.590
298	1.2198	0.9342	8.82	0.590
303	1.2018	0.9298	8.82	0.590
		Isovaleric acid		
288	1.2020	0.9344	8.23	0.594
293	1.1839	0.9301	8.23	0.594
298	1.1658	0.9261	8.23	0.594
303	1.1480	0.9219	8.23	0.594
		Caproic acid		
298	1.2569 d)	0.9225	8.80	0.533
303	1.2405	0.9183	8.80	0.533
308	1.2233	0.9135	8.80	0.533
313	1.2064	0.9092	8.80	0.533
318	1.1876	0.9049	8.80	0.533

a), b), c) The values calculated from H. H. Landolt and R. Bornstein, "Physikalische Chemische Tabellen," Vol. III. Part 3. d) The sound velocities measured at 5 MHz.

±10% respectively.

If one assumes that the excess absorption in a series of monocarboxylic acids is due to the same type of reaction as in the case of acetic2) and propionic4) acids, the general expression for this reaction type is:

$$A \underset{k_b}{\overset{k_f}{\rightleftarrows}} B$$

and:

$$K = \frac{k_f}{k_b} \qquad (2)$$

$$2\pi f_{\max} = k_f + k_b \qquad (3)$$

where K is the equilibrium constant and where k_f and k_b are the forward and backward rate constants respectively. If it is assumed that the volume change in this reaction is zero, the relaxation heat capacities at a constant volume and pressure are represented by the equation:

$$C_p^r = C_v^r = \frac{(\varDelta H)^2}{RT^2} \cdot \frac{K}{(1+K)^2} \qquad (4)$$

where $\varDelta H$ is the enthalpy change of reaction; T, the absolute temperature, and R, the gas constant.

The enthalpy change is calculated by means of van't Hoff's isochore:

$$\left(\frac{\partial \ln K}{\partial(1/T)}\right)_p = -\frac{\varDelta H}{R} \qquad (5)$$

$$K = \exp\left(-\varDelta G/RT\right) \qquad (6)$$

where $\varDelta G$ is the free energy change of the reaction. Similarly, the temperature dependence of the rate constant is given by:

$$\left(\frac{\partial \ln k}{\partial(1/T)}\right)_p = -\frac{\varDelta H^{*}}{R} \qquad (7)$$

The activation free energy is given by the Eyring equation:

$$k = \frac{kT}{h} \exp\left(-\frac{\varDelta G^{*}}{RT}\right) \qquad (8)$$

where k is the Boltzman constant; h, the Planck constant, and $\varDelta G^{*}$, the activation free energy. The kinetic parameters, K, k_f, and k_b, and thermodynamic parameters, $\varDelta H$ and $\varDelta H^{*}$, were calculated from Eqs. (2)—(6) by the same procedure as was used in a previous paper.4) $\varDelta G$ and $\varDelta S$ were calculated by the relationship: $\varDelta G = \varDelta H - T\varDelta S$. The values thus obtained are listed in Table 3. The uncertainties in K, $\varDelta G$, $\varDelta H$, $\varDelta S$, k_b, k_f, $\varDelta H_b^{\ddagger}$, and $\varDelta H_f^{\ddagger}$ are approximately ±30, ±20, ±20, ±20, ±5, ±10, ±10, and ±20% respectively.

Discussion

As can be seen in Table 3, $\varDelta H$ increases monotonously with the increase in the carbon number for normal compounds, while it decreases for isocompounds. In order to explain this phenomenon quantitatively from the point of view of the structure of the alkyl group, the following Taft's9) equation is used:

TABLE 3. THE KINETIC PARAMETERS FOR A SERIES OF MONOCARBOXYLIC ACIDS AT 30°C

	K (10^{-2})	$\varDelta G$ $\left(\frac{\text{kcal}}{\text{mol}}\right)$	$\varDelta H$ $\left(\frac{\text{kcal}}{\text{mol}}\right)$	$\varDelta S$ $\left(\frac{\text{cal}}{\text{deg}}\right)$	k_b $\left(\frac{10^7}{\text{sec}}\right)$	$\varDelta H_b^{\ddagger}$ $\left(\frac{\text{kcal}}{\text{mol}}\right)$	k_f $\left(\frac{10^5}{\text{sec}}\right)$	$\varDelta H_f^{\ddagger}$ $\left(\frac{\text{kcal}}{\text{mol}}\right)$
Acetic acid a)	21.9	0.95	2.7	5.9	0.47	8.9	10.3	~12
Propionic acid b)	3.3	2.0	4.3	7.3	1.7	6.8	5.9	~11
Butyric acid	3.0	2.1	4.7	8.5	1.5	5.3	4.6	~10
Valeric acid	1.4	2.5	5.4	9.3	2.7	5.5	3.9	~10
Caproic acid	1.0	2.7	5.7	9.7	2.3	6.0	2.3	~11
Isobutyric acid	0.35	3.3	6.4	9.9	5.5	5.0	1.9	~12
Isovaleric acid	0.74	2.9	6.0	10.0	3.0	5.8	2.2	~12

a), b) The values calculated from data in literatures.2,4)

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9) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 2729 (1952).

$$\log K_i = \rho^*\sigma^* + sE_s \qquad (9)$$

where K_i is the rate constant or equilibrium constant; σ^*, the polarity parameter, and E_s, the steric parameter. ρ^* and s are proportionality constants and depend only on the type of reaction. The plots of $\log K$ against σ^* and E_s are represented in Figs. 7 and 8 respectively, where for the values of σ^* and E_s those found in the literature are used.9,10) It can be seen in the figures that $\log K$ changes linearly with σ^*, while no simple relationship is found between $\log K$ and E_s. The value of ρ^* calculated from the plot is 13.8. From this fact and the linearity between $\log K$ and ΔH, as can be seen in Fig. 9, it can be deduced that the difference in the ΔH values of the series of monocarboxylic acids is due to variations in the polarity effect of each alkyl group in the molecules. A combination of Figs. 7 and 8 shows that ΔH increases with the strength of the polarity effect, *i.e.*, with the decrease in σ^*. The values of ΔH are in the range of 4.7—6.4 kcal per mole of dimer; this finding is consistent with the fact that these values are those of the breaking of one hydrogen bond, and there is a linear relationship11) between σ^* and the inductive effect of the alkyl group on the carboxyl group. From these

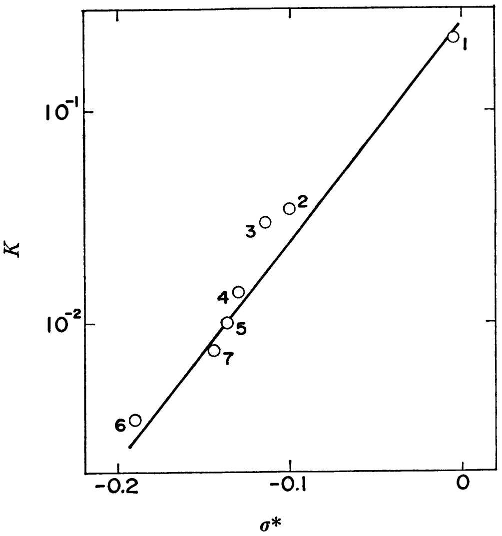

Fig. 7. The plot of ln K against σ^* for a series of carboxylic acids. Hereafter numbers denote the acids as (1), acetic; (2), propionic; (3), butyric: (4), valeric; (5), caproic; (6), isobutyric; and (7), isovaleric acids.

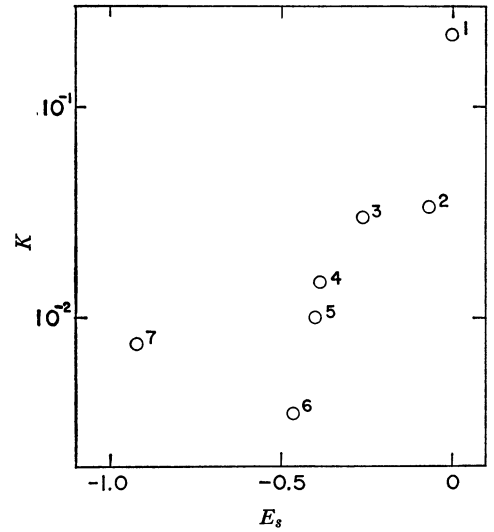

Fig. 8. The plot of ln K against E_s.

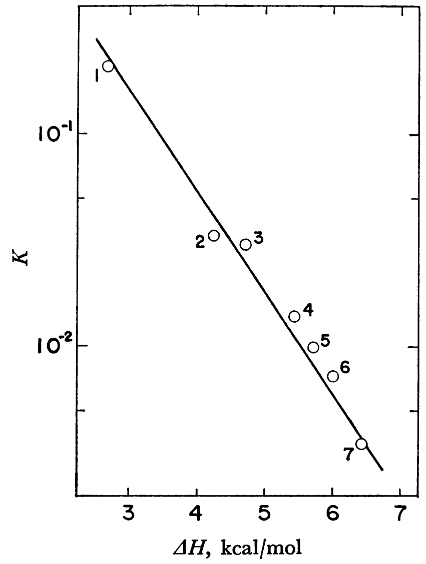

Fig. 9. The plot of ln K against ΔH.

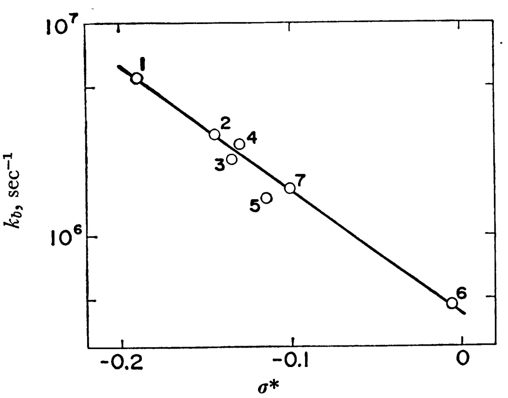

Fig. 10. The plot of ln k_b against σ^*.

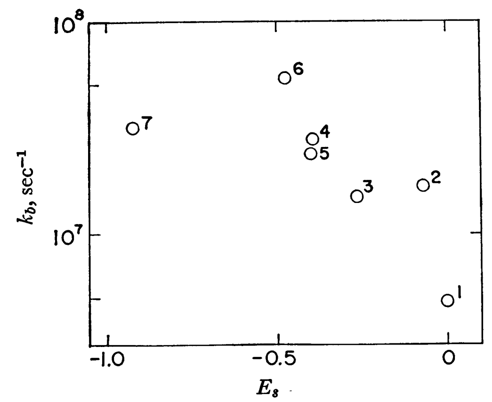

Fig. 11. The plot of ln k_b against E_s.

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10) R.W. Taft, Jr., *J. Amer. Chem. Soc.*, **75**, 4538 (1953).

11) M. Chiang and T. Tai, *Scientia Sinica*, **12**, 785 (1963).

results, it can be concluded that the electron density of the carboxyl group increases with the increase in the inductive effect, so the hydrogen bond becomes more stable in the cyclic dimer than in the open dimer.

The relationships between the rate constant and the values of σ^* and E_s, are shown in Figs. 10 and 11, where the plot of $\log k_b$ against σ^* gives a straight line; no such relationship exists between $\log k_b$ and E_s, however the value of ρ^* calculated from the plot is -7.90. The change in $\Delta H_b^\ddagger$ cannot, however, be ascribed to the polarity effect, as can be seen in Table 3, where there exists no simple relationship between $\log k_b$ and $\Delta H_b^\ddagger$.

As can be seen in Table 3, the $\Delta H_b^\ddagger$ values of acetic and propionic acids are greater than those of other acids. The abnormal $\Delta H_b^\ddagger$ values of these two acids may be ascribed to the formation of the polymer, as has been suggested by a study[12] of sound velocity and dipole moment. The liquid contains some linear polymer, and some excess energy is required to break the hydrogen bonds of the polymer.

From the above discussion, it may reasonably be concluded that the excess absorptions in the series of monocarboxylic acids are all associated with the perturbation of the equilibrium between the open dimer and the cyclic dimer, and that the cyclic dimer becomes more stable because of the inductive effect of the alkyl group, which increases the electron density in the carboxyl group.

More extensive measurements may be desirable to confirm the inductive effect mentioned above. A study of halogeno carboxylic acids is now in progress; the results will be reported.

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[12] M. Blinc and R. Blinc, *J. Polym. Sci.*, **32**, 506 (1958).